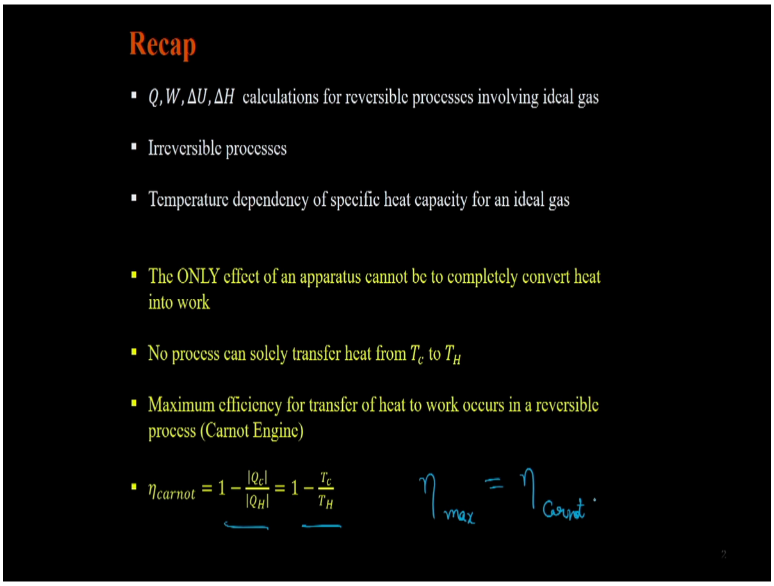
Chemical Engineering Thermodynamics
Prof. Sasidhar Gumma
Department of Chemical Engineering
Indian Institute of Technology, Guwahati

Lecture – 08
Second Law and Entropy

Hello and welcome back; in the last class we were looking at the second law of thermodynamics and Carnot cycles; which essentially form the backbone for the second law of thermodynamics.

(Refer Slide Time: 00:51)



Recap

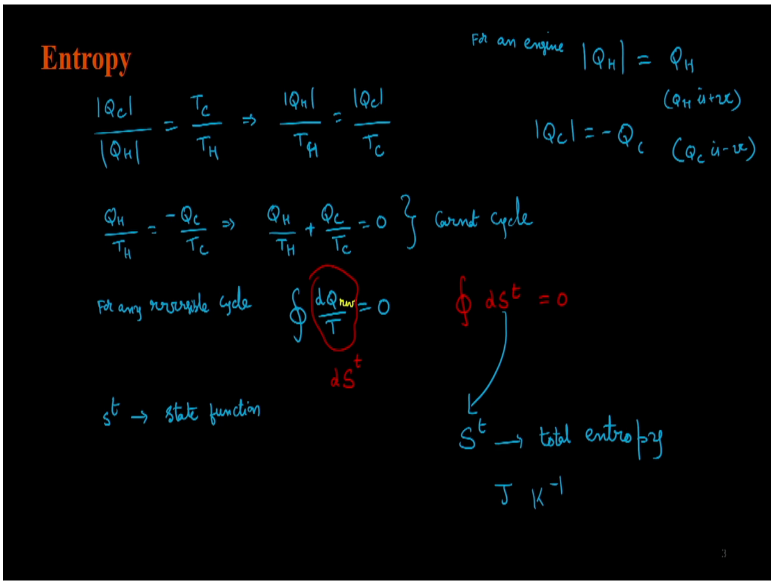
- $Q, W, \Delta U, \Delta H$ calculations for reversible processes involving ideal gas
- Irreversible processes
- Temperature dependency of specific heat capacity for an ideal gas
- The ONLY effect of an apparatus cannot be to completely convert heat into work
- No process can solely transfer heat from T_c to T_H
- Maximum efficiency for transfer of heat to work occurs in a reversible process (Carnot Engine)
- $\eta_{carnot} = 1 - \underline{\frac{|Q_c|}{|Q_H|}} = 1 - \underline{\frac{T_c}{T_H}}$ $\eta_{max} = \eta_{Carnot}$.

Let us quickly recap what we have done. So, far we have looked at the heat work requirements and change in enthalpy and internal energy for a process that involves ideal gas. We looked at irreversible processes and how to account for that irreversibility through defining the efficiency of the irreversible process. We also looked at the temperature dependency for heat capacity of an ideal gas and then we started looking at second law of thermodynamics and we said that we cannot be learn apparatus which can completely convert heat into work.

And we also defined what is known as a Carnot engine and it turns out that the conversion from heat to work occurs in the maximum conversion for heat to work occurs for a reversible process. And if we build an engine around this reversible process; we call that as a Carnot engine and the efficiency of the Carnot engine is given by these relations down here right. It is 1 minus Q C over Q H that is the ratio of the heat transferred for to the cold reservoir and heat taken from the hot reservoir. And it turns out that we can show that this ratio will also be equal to the temperatures of the two reservoirs.

So, the efficiency is going to be 1 minus T C by T H. And again like I said we want to note this, the maximum efficiency we can obtain is for a process that involves a Carnot engine. Now let us look at the definition of another thermodynamic variable which we call as law of entropy.

(Refer Slide Time: 02:26)



Entropy

$\frac{|Q_c|}{|Q_H|} = \frac{T_c}{T_H} \Rightarrow \frac{|Q_H|}{T_H} = \frac{|Q_c|}{T_c}$

For an engine $|Q_H| = Q_H$

(Q_H is +ve)

$|Q_c| = -Q_c$ (Q_c is -ve)

$\left.\frac{Q_H}{T_H} = \frac{-Q_c}{T_c} \Rightarrow \frac{Q_H}{T_H} + \frac{Q_c}{T_c} = 0\right\}$ Carnot cycle

For any reversible cycle $\oint \underbrace{\frac{dQ_{rev}}{T}}_{dS^t} = 0$

$\oint dS^t = 0$

$S^t \rightarrow$ state function

$S^t \rightarrow$ total entropy

$J\ K^{-1}$

Now, recall that we have demonstrated that the ratio of the heat exchange with the cold and hot reservoirs is equal to T C over T H. And what this implies is Q H by T H; H is Q C over T C and remember we are talking about a engine here. For an engine Q H is the absolute value is going to be equal to Q H; since Q H is positive. And for Q C this would be negative of Q C because Q C is negative. So, the absolute value is going to be negative of negative which is going to be positive. So, absolute value in that sense is negative of QC.

So, if I take this and put it back here it turns out then Q H over T H is going to be equal to negative of Q C over T C; these are the actual values not the absolute values. And what this implies is Q H over T H plus Q C over T C would equal 0 this is true for any Carnot cycle.

So, if I complete the cycle right the total amount of the ratios of Q to T over the hot reservoir and the cold reservoir; if I add them up it should go to 0. Now it turns out for any reversible process again this can be proved thermodynamically, but we will take it as it is it turns out that for any reversible process or if we actually talk about the cycle any reversible cycle can be produced by a series of closely spaced Carnot cycles.

So, any reversible cycle can actually be built from a series of Carnot cycles depending on how we arrange them, but they need to be closely spaced. So, if that be the case for any reversible cycle; the integral the cyclic integral d Q over T will be equal to 0. This is because a reversible cycle is made up of constituent small Carnot cycles and for a Carnot cycle; we have already demonstrated that Q H by T H plus Q C by T C is 0.

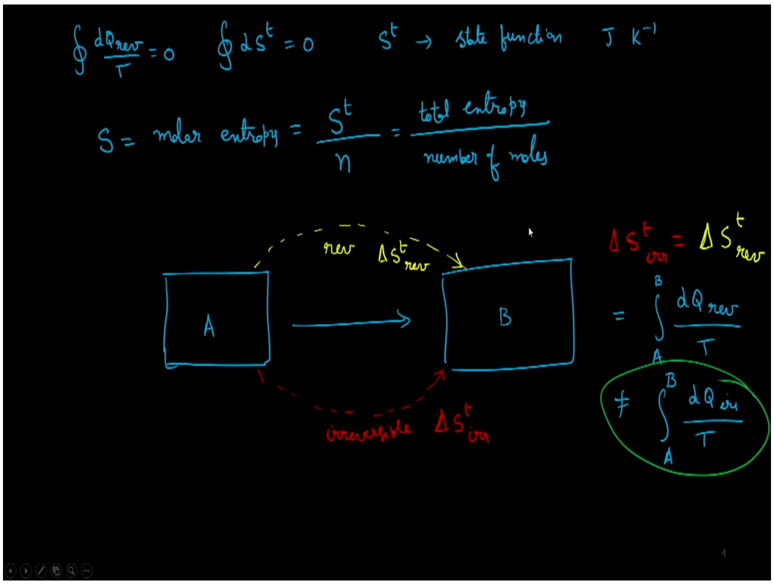
So, if you complete the cycle for a Carnot cycle Q by T is 0 and because the reversible cycle can be produced from a series of Carnot cycles; this cyclic integral of d Q over T will be equal to 0. So, to make the point that we are talking only about irreversible cycle; let us write that that this d Q needs to be for a reversible cycle. What we will do is; we will replace this as we always do we will replace this quantity d Q reversible over d T with d S and because this is total let us call it as d S t.

So, then this cyclic integral over d S t will be equal to 0 and this quantity S t is called as the total entropy. And because the units are energy per temperature; we can think of it as in case of SI units it would be Joule per temperature which is Kelvin. So, S t is called as the total entropy its units are going to be Joule per Kelvin and the cyclic integral over S t for any reversible process so far is going to be equal to 0.

Now if you think about it we said that d S t equals 0 right and I can make because I can make it for any reversible process; it turns out that d S t actually will be a state function or rather S t will be a state function. That is because I can build several reversible cycles and all of them will give me the same change in the entropy. So, S t itself will be a state function it will not be dependent on what path I take to reach that particular state.

So, because S t is a state function, it turns out that I can actually irrespective of the path whether reversible or irreversible; the change in entropy is always going to be same.

(Refer Slide Time: 07:59)



$\oint \frac{dQ_{rev}}{T} = 0$ $\oint dS^t = 0$ $S^t \rightarrow$ state function J K^{-1}

$S =$ molar entropy $= \frac{S^t}{n} = \frac{\text{total entropy}}{\text{number of moles}}$

$\Delta S^t_{irr} = \Delta S^t_{rev}$

$= \int_A^B \frac{dQ_{rev}}{T}$

$\neq \int_A^B \frac{dQ_{irr}}{T}$

We will come back to that in a minute, but over here let us summarize then what we discussed so far. We said the cyclic integral of d Q reversible over T is 0 and we call this as d S t is 0 and S t is a state function. And the units are going to be Joules per Kelvin; I can define in S, which is the molar entropy. And as usual our definition for molar quantity is going to be the total entropy over the number of moles; total entropy S t over the number of moles.

Now, since S t is a state function let us say I have a process going from A to B state; A to state B. And I can build two paths; so for this process a reversible path where the change in entropy is going to be delta S t reversible and an irreversible path; where the change in entropy is going to be delta S t irreversible.

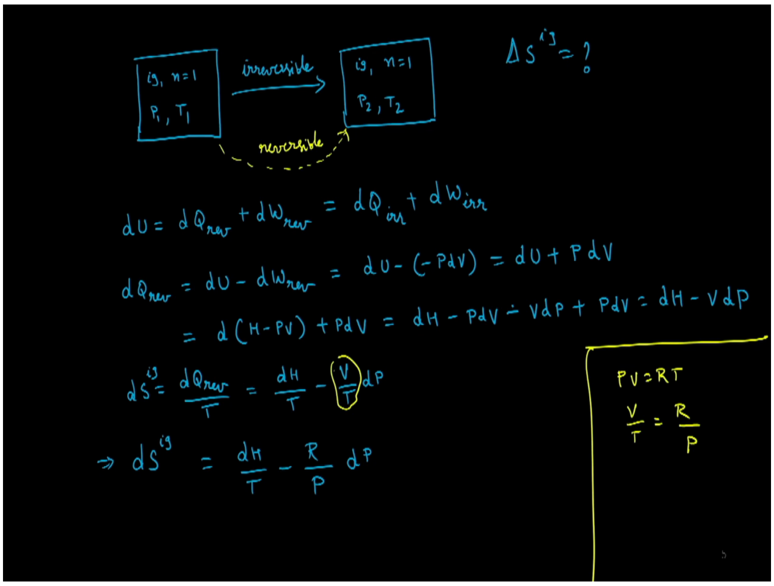
And because S t is we said is a state function right delta S t over the irreversible path is going to be equal to delta S t over the reversible path. And both these quantities if I want to relate them to the heat requirements will integral of d Q reversible going from A to B over T. And this will not be equal to the d Q over T of the irreversible path. Remember Q itself is dependent on the path; so Q for reversible and irreversible paths is different.

So, if we integrate that d Q irreversible over T here; this quantity then it does not give us entropy. But if we integrate it over the reversible path, it will give us the change in entropy and irrespective of the path whether reversible or irreversible the change in entropy is going to be same because we are talking about a state function here in this case entropy.

Now let us talk about then; so we defined now from the second law we defined a quantity called as entropy based on our idea of the second law. And it turns out that entropy is a state function and irrespective of whether the actual process is reversible or irreversible; I can always calculate the change in entropy by considering the heat requirement for a reversible path.

Now, let us talk about its implications in calculation of entropy. Let us say I have an ideal gas we; so far our discussion is for ideal gases we know; how to make heat and work requirement calculations for processes that involve ideal gas.

(Refer Slide Time: 11:23)



$$\Delta S^{ig} = ?$$

$$dU = dQ_{rev} + dW_{rev} = dQ_{irr} + dW_{irr}$$

$$dQ_{rev} = dU - dW_{rev} = dU - (-PdV) = dU + PdV$$

$$= d(H - PV) + PdV = dH - PdV - VdP + PdV = dH - VdP$$

$$dS^{ig} = \frac{dQ_{rev}}{T} = \frac{dH}{T} - \frac{V}{T}dP$$

$$\Rightarrow dS^{ig} = \frac{dH}{T} - \frac{R}{P}dP$$

$$PV = RT$$

$$\frac{V}{T} = \frac{R}{P}$$

So, we will stick to that let us say I have an ideal gas, I have one mole of ideal gas and the temperature and pressure are P 1 and T 1 initially; I go to it is a closed system. So, n is still 1 and the final temperature and pressure are P 2 and T 2. And we want to calculate the change in entropy for this process this is ideal gas of course, what is the change in entropy if this was given to me right.

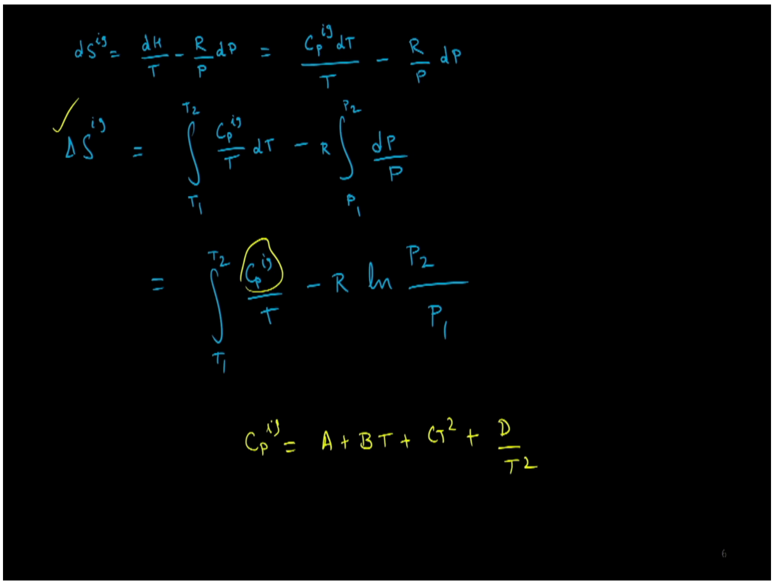
Now we do not know. Let us say this is an irreversible path and we want to calculate the change in entropy for this, but entropy is a state function. So, what I can do is I can always construct a reversible path for this process right. I have constructed a reversible path right; now over this reversible path; now if you recall d U the change in internal energy is d Q for the reversible plus d W for the reversible path. And they should also equal d Q for the irreversible plus d W for the irreversible; both Q and W are dependent on the path whereas, d U is not dependent or U is not dependent. Because again just like entropy is a state function we already talked about this right.

Now, for a reversible process d Q reversible is then d U minus d W for the reversible process and for a reversible process we already know that d W is negative P d V. So, this is d U plus P d; this is d Q for the reversible process right. And we are doing this because we want to express everything in terms of specific heat capacities d U's or d H's; so that I can express entropy also in terms of specific heat capacity.

So, what we will do is change d U because we like C P ij more it is just convenient to use that when I say like. So, we will change this H minus PV plus P d V and now would be d H minus P d V minus V d P plus P d V and that will be d H minus V d P right d H minus V d P. This is d Q reversible; now d S we know is d Q reversible over T; so that will be d H over T minus V over T d P; V over T d P right; this is the yes.

So, what we can do is this is an ideal gas right let us write that in a separate color. So, that we know what we are doing just for sake of it; V over T for an ideal gas is well PV is RT right for an ideal gas; PV is RT. So, V over T is R over P. So, I am going to replace this guy here with R over P; let us do that so that what I get is d H over T minus; R over P d P R over P d P. So, this is my d S well of course, this is for an ideal gas; so let us not forget that superscript there; so, this is d S ig.

(Refer Slide Time: 15:24)



$$dS^{ig} = \frac{dH}{T} - \frac{R}{P}dP = \frac{C_p^{ig}\,dT}{T} - \frac{R}{P}dP$$

$$\checkmark\ \Delta S^{ig} = \int_{T_1}^{T_2} \frac{C_p^{ig}}{T}dT - R\int_{P_1}^{P_2}\frac{dP}{P}$$

$$= \int_{T_1}^{T_2} \frac{C_p^{ig}}{T} - R\ln\frac{P_2}{P_1}$$

$$C_p^{ig} = A + BT + CT^2 + \frac{D}{T^2}$$

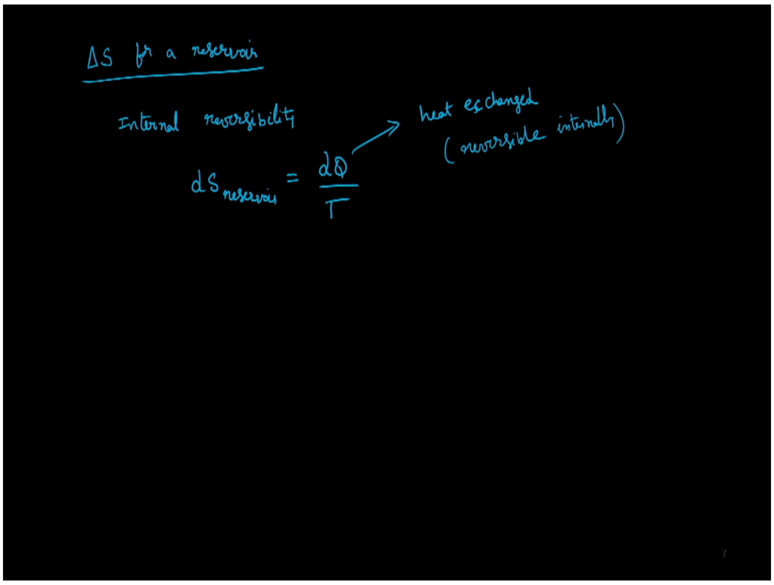
Now, if I want delta S; let us write that again d S ig is d H over T minus R over P d P. Now, d H if you remember is C P for the ideal gas d T; it is only dependent on temperature.

So, its C P d T minus R over P d P; if I want delta S ig then it will be integral T 1 to T 2 this is integral for T. So, its C p ig by T d T minus integral R there; P 1 to P 2 d P over P. So, that will be integral T 1 to T 2 C p ig by T minus R ln P 2 over P 1. So, this is the change in entropy than expressed in terms of the specific heat capacity for the ideal gas and the change in pressures.

Now if I have the temperature and pressure and I know the specific heat capacity or the functionality for specific heat capacity. If you recall one of the expressions we used is BT plus CT square plus D by T square right; it is a function of temperature. I can substitute this functionality of temperature and if I know the parameters A B C and D, I should be able to calculate that integral and if I know T 1 and T 2 P 1 and P 2, then I can calculate the change in entropy at least for him as far as an idea of gas is concerned right.

So, then what we have done is defined the; a quantity a new thermodynamic variable called as entropy and we looked at how we can perform the calculation for change in entropy in case of an ideal gas.

(Refer Slide Time: 17:31)



ΔS for a reservoir

Internal reversibility

$$dS_{reservoir} = \frac{dQ}{T}$$

→ heat exchanged (reversible internally)

One of the important things; we will encounter as we go on is calculating delta S for a reservoir. What is change in entropy for a reservoir? Now, if you recall our definition when we say reservoir what we mean is it is an infinite source of heat or a sink of heat.

So, if we are rejecting heat to the reservoir; it will be an infinite source of a sink for heat. And if we are accepting heat from the reservoir it is an infinite source of heat. In that sense the temperature of the reservoir because we are adding additional heat is not going to change much; it is going to be what it is an infinite source. So, even if we add this my minute amount of heat or remove minute amount of heat from this infinite source; it is not going to change much.

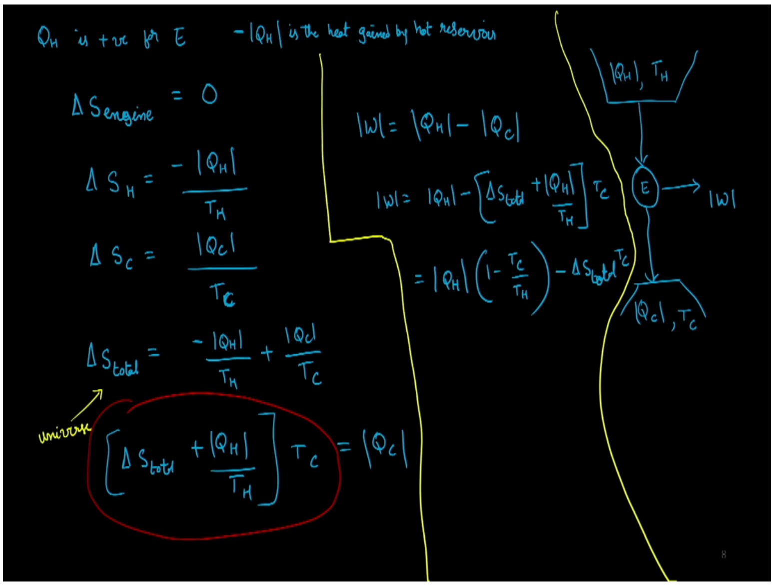
The temperature is not changing then the gradients for temperature within the reservoir are negligible; they are very well they are actually 0 if it is infinite source, but if it is a very large source which is practically getting an infinite source is not possible, but if it is very large source then the gradients for the temperature within the reservoir are going to be minimal very negligible. And if the gradients are negligible then we approach; remember, when we define irreversibility for the process with the example of a piston cylinder simply taking weights of the load from the piston and replace it with grains of sand which are very very small; we are actually reducing the gradients.

And in this case the only thing that matters is the temperature gradient and because a reservoir is an infinite source; the temperature gradients within the reservoir are negligible. And once the temperature gradients are negligible the process is going to approach reversibility. So, at least as far as the reservoir alone is concerned; it approaches what we call as internal reversibility because the temperature gradients internally within the reservoir are negligible.

If it approaches internal reversibility then for calculation of the entropy change in the reservoir right d S for the reservoir is going to be d Q over T; where this d Q is the heat exchanged. And because it is internally reversible it does not matter what is happening outside the reservoir, but the moment we say reservoir is exchanging a heat of d Q either positive or negative; then d S is simply d Q over T because internally as far as the reservoir alone is concerned it has exchanged a heat of d Q. So, d S reservoir is going to be d Q over T because this d Q is a heat that is exchanged reversibly right.

So, it is simply going to be d Q over T. So, when we do this although the process itself might be externally reversible only as far as the reservoir is concerned; the change in entropy is always going to be d Q over T. Now let us talk about the implications of entropy and how we calculate the efficiency of a process or the work extracted from an engine using the concept of entropy. So, for that let us consider a engine.

(Refer Slide Time: 21:21)



Q_H is +ve for E $-|Q_H|$ is the heat gained by hot reservoir

$$\Delta S_{engine} = 0$$

$$\Delta S_H = \frac{-|Q_H|}{T_H}$$

$$\Delta S_C = \frac{|Q_C|}{T_C}$$

$$\Delta S_{total} = \frac{-|Q_H|}{T_H} + \frac{|Q_C|}{T_C}$$

universe

$$\left[\Delta S_{total} + \frac{|Q_H|}{T_H}\right] T_C = |Q_C|$$

$$|W| = |Q_H| - |Q_C|$$

$$|W| = |Q_H| - \left[\Delta S_{total} + \frac{|Q_H|}{T_H}\right] T_C$$

$$= |Q_H|\left(1 - \frac{T_C}{T_H}\right) - \Delta S_{total} T_C$$

So, I have in case of an engine what I have is a reservoir from which I accept heat; that heat goes into the engine. And this engine outputs a work which is equal to W and rejects some heat to the cold reservoir at T C; this is my engine.

Now based on our notation Q H is positive for the engine; well let us just say Q H like that and negative Q H is the. So, when I take the absolute value of Q H it is positive. So, negative of this absolute value of Q H is the heat gained by hot reservoir in its; in a sense it is a negative quantity; so it is the heat lost by hot reservoir.

Now, let us say we go through a complete cycle where I start with the indish; the engine in a particular state I accept heat, output work reject the heat and go back to its initial state; so I complete the whole process. Once I complete the whole cycle the change in the entropy for the engine is going to be equal to 0 because I completed the cycle; I came back to where I was; S is a state function. So, the change in entropy for the engine is 0.

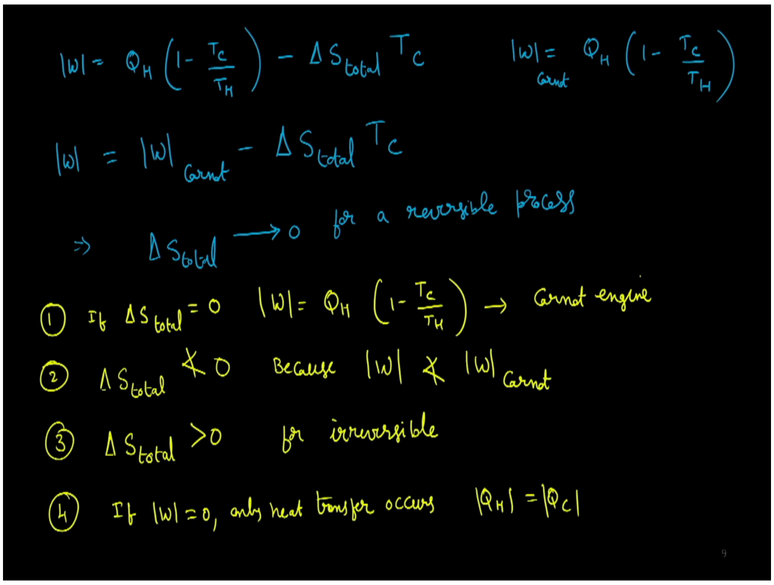
On the other hand, the change in entropy of the hot reservoir is going to be equal to negative of Q H or T H; Q H is the heat it is well the reservoir is rejecting heat to the engine the engine is accepting it from the reservoir. So, absolute value of Q H is the heat that is rejected by the engine. So, negative of that quantity is the heat that the reservoir is gaining from the engine. So, that change in entropy as we have discussed in the previous slide; as far as the reservoir is concerned is Q H over T H because reservoir itself is it internally reversible.

So, now the total change in entropy for when I say total; we mean total for the universe and in this case the universe constitutes the engine and the two reservoirs. So, the total change in the entropy is essentially negative of 0; the first quantity for the engine anyway then negative of Q H by T H plus Q C over T C; this is a total change in the entropy of the universe.

And as far as the work done is concerned; it is going to be, if we do a balance energy balance over the engine or the first law over the engine the W has to be equal to Q H minus Q C right. I can do a little bit of manipulation here for this delta S total plus Q H over T H multiplied with T C; this will equal to Q C right. What I will do is take this quantity right here and substitute it for this Q C there right.

And if I do that right; let us go back to that. I am going to take this quantity; then W is going to be Q H minus delta S total plus Q H over T H times T C. And if I simplify this; this will be Q H 1 minus T C over T H minus delta S total times T C right. So, what I have is an expression for work done; it is Q H 1 minus T C by T H minus delta S total times T C.

(Refer Slide Time: 26:36)



$|W| = Q_H\left(1 - \frac{T_C}{T_H}\right) - \Delta S_{total} T_C$ $\qquad |W|_{Carnot} = Q_H\left(1 - \frac{T_C}{T_H}\right)$

$|W| = |W|_{Carnot} - \Delta S_{total} T_C$

$\Rightarrow \quad \Delta S_{total} \longrightarrow 0$ for a reversible process

① If $\Delta S_{total} = 0$ $\quad |W| = Q_H\left(1 - \frac{T_C}{T_H}\right) \rightarrow$ Carnot engine

② $\Delta S_{total} \nless 0$ Because $|W| \ngtr |W|_{Carnot}$

③ $\Delta S_{total} > 0$ for irreversible

④ If $|W| = 0$, only heat transfer occurs $|Q_H| = |Q_C|$

Now, let us go back and rewrite this expression one more time this is an important observation, it turns out W is Q H 1 minus T C over T H right minus delta S total times T C right. Now remember, the work done for a Carnot engine; which is the ideal scenario for a reversible process is Q H 1 minus T C over T H.

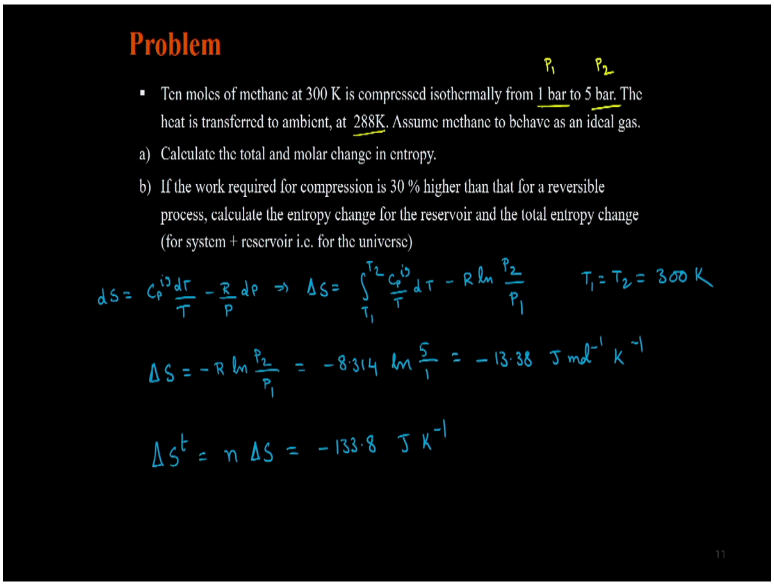
So, then this W is the W for the Carnot engine minus delta S total times T C. What this implies is delta S total; we all go to 0 for a Carnot engine or for a reversible process. So, if the process itself is reversible, then the total change in entropy has to be equal to 0.

Let us summarize then; if delta S total, the total change in entropy for the system and the surroundings or the total change in entropy of the universe is 0; then the work done is Q H 1 minus T C by T H; which is that of a Carnot engine. Secondly, delta S total can never be less than 0 because if it is less than 0; then this W here right.

Because if this is less than 0 W is never greater than the W for the Carnot engine because Carnot engine has the maximum one can obtain the maximum work done in case of a Carnot engine. So, we cannot violate that second law requirement and then for a irreversible process delta S total is going to be greater than 0 for irreversible process. We talked about reversible process, we talked about the scenario that it cannot be less than 0. So, the only thing that is left is that it is going to be greater than 0 for an irreversible process.

And the fourth point we want to make is that when the total work output from the process is 0; which is the scenario when W is 0 then we are not out there is no output of work; what occurs is only heat transfer from the hot reservoir to the cold reservoir right. And in such a scenario; obviously, we can go through the math, but it turns out that Q H should be equal to Q C. And we can obtain an expression for the change in entropy for such a process etcetera, it is going to be maximum for such a scenario.

(Refer Slide Time: 29:36)



Problem

P_1 P_2

- Ten moles of methane at 300 K is compressed isothermally from 1 bar to 5 bar. The heat is transferred to ambient, at 288K. Assume methane to behave as an ideal gas.

a) Calculate the total and molar change in entropy.

b) If the work required for compression is 30 % higher than that for a reversible process, calculate the entropy change for the reservoir and the total entropy change (for system + reservoir i.e. for the universe)

$$dS = C_p^{ig} \frac{dT}{T} - \frac{R}{P} dP \Rightarrow \Delta S = \int_{T_1}^{T_2} \frac{C_p^{ig}}{T} dT - R \ln \frac{P_2}{P_1} \qquad T_1 = T_2 = 300\ K$$

$$\Delta S = -R \ln \frac{P_2}{P_1} = -8.314 \ln \frac{5}{1} = -13.38\ J\ mol^{-1}\ K^{-1}$$

$$\Delta S^t = n\,\Delta S = -133.8\ J\ K^{-1}$$

Let us look at an example we have 10 moles of methane at 300 Kelvin and it is being compressed isothermally from 1 bar to 5 bar. The heat is transferred to the ambient at 288 Kelvin; assume methane behaves as an ideal gas. We want to calculate the total and the molar change in entropy. And we also want to calculate the entropy change for the reservoir and the total entropy change for the universe; if the work required for compression is 30 percent higher than that of a reversible process. Let us see how we can solve this particular problem.

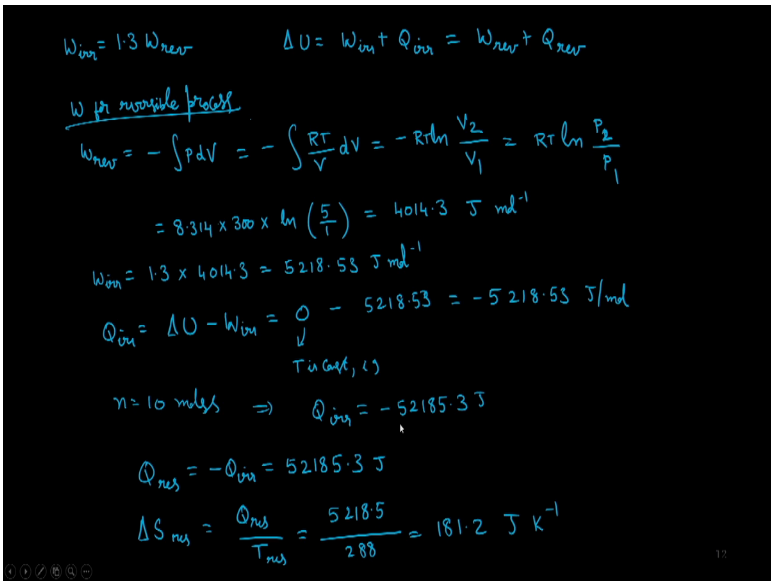
So, I have P 1 and P 2 given to me the first thing is pretty straightforward; we have an ideal gas and we want to calculate the total and molar change in the entropy for this particular process. Now, if you recall we have derived the expression for entropy change of an ideal gas and we said it is d S is C P; ig d T over T minus R by P d P or delta S is integral T 1 to T 2 C p ig by T; d T minus R ln P 2 over P 1.

In this case, we are compressing methane isothermally right. So, this isothermal compression essentially means for methane itself the temperature is not changing. So, T 1 equals T 2 equals 300 Kelvin and in which case the first part of the delta S or the first term in the delta S cancels out; there is no integral of T 1 to T 2 it will go to 0, all I am left with is minus R ln P 2 over P 1.

And if I put consistent units what I will have is minus 8.314 SI units of Joule per mole per Kelvin; ln of 5 over 1 that will give me negative 13.38 Joule per mole per Kelvin. Remember total entropy has units of Joule per Kelvin; molar entropy has units of Joules per mole per Kelvin, this is the molar enthalpy change if am interested in the total entropy change, then it is the number of moles multiplied with the molar value.

So, that would be negative 133.8 this case the units are going to be Joules per Kelvin; this is how we calculate the entropy change. Now the second part of the problem says we know that the process is irreversible and the work required for the irreversible compression is 30 percent higher than that for the reversible compression. We want to calculate the entropy change for the reservoir and for the total entropy change for such a process; let us see how we can do that.

(Refer Slide Time: 31:52)



$W_{irr} = 1.3\, W_{rev}$ $\Delta U = W_{irr} + Q_{irr} = W_{rev} + Q_{rev}$

W for reversible process

$$W_{rev} = -\int P\,dV = -\int \frac{RT}{V}\,dV = -RT\ln\frac{V_2}{V_1} = RT\ln\frac{P_2}{P_1}$$

$$= 8.314 \times 300 \times \ln\left(\frac{5}{1}\right) = 4014.3\ \text{J mol}^{-1}$$

$$W_{irr} = 1.3 \times 4014.3 = 5218.53\ \text{J mol}^{-1}$$

$$Q_{irr} = \Delta U - W_{irr} = \underset{\substack{\downarrow \\ T \text{ is Const, i.g}}}{0} - 5218.53 = -5218.53\ \text{J/mol}$$

$$n = 10 \text{ moles} \Rightarrow Q_{irr} = -52185.3\ \text{J}$$

$$Q_{res} = -Q_{irr} = 52185.3\ \text{J}$$

$$\Delta S_{res} = \frac{Q_{res}}{T_{res}} = \frac{5218.5}{288} = 181.2\ \text{J K}^{-1}$$

So, let us write this down we are given that the W the work requirement for the irreversible process is 30 times higher. So, it is going to be 1.3 times W for the reversible process and we also know that delta U has to be same irrespective of the path; which means delta U is going to be W plus Q for irreversible process which is going to be same as W plus Q for the reversible process.

So, what we will do then is first find W for the reversible process; W reversible if you recall is negative integral of P d V; that is going to be negative integral because this is an ideal gas, methane behaves as an ideal gas that is given to us d V; it is a isothermal process the temperature is constant. So, it is going to be negative R ln V 2 over V 1 right negative R ln V 2 over V 1. So, this will be we do not know the temperatures, but we know the pressure.

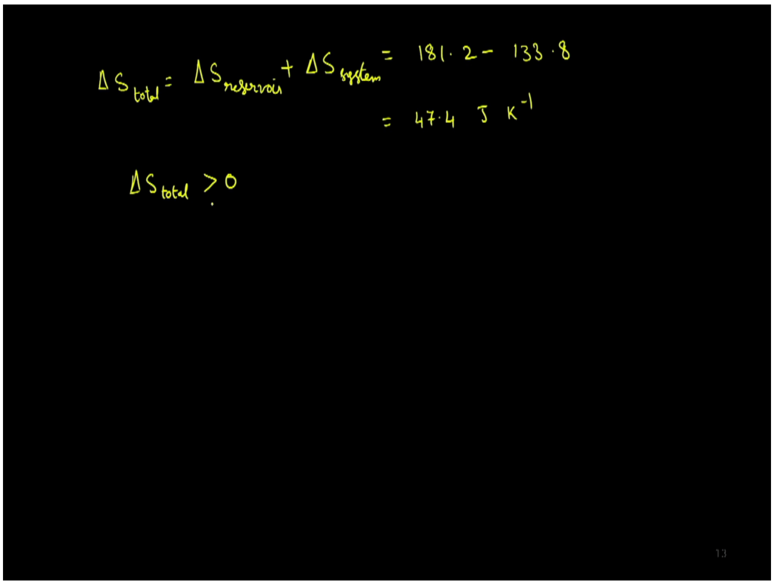
So, I can easily flip that ratio of volumes to ratio of pressures and it will be negative of that R ln P 2 over P 1. So, that is going to be 8.314 logarithm of 5 over 1; I am sorry there is an RT term there. So, this is RT ln P 2 over P 1. So, that is going to be 8.314 times 300 times ln of 5 over 1; so, that will be 4014.3 Joules per mole. This is the work requirement for a reversible process per mole of course, right. Now for an irreversible process the work requirement is 30 times higher; so it will be 1.3 times of this quantity.

So, which will be 5218.53 Joules per mole right and W for the, we calculated W for the irreversible process. Now if you think about it Q for the irreversible process is going to be delta U minus W for the irreversible process. Delta U is 0 because T is constant and it is an ideal gas minus 5218.53. So, delta U is 0 because we have an ideal gas and the temperature is not changing; so, change in an internal energy is 0.

So, Q then will essentially be negative of W which will be 5218.53 Joule per mole; this will be Q for the irreversible process right. And I have 10 moles of the gas; so the total Q for the irreversible process is going to be negative 52185.3; 10 times of that value molar value. So, it will be negative 52185.3 Joules. As far as the reservoir is concerned, it will be negative of what this value is.

So, the methane in this case is losing heat; so the reservoir is going to gain that heat so, that quantity is going to be positive so many Joules. And delta S for the reservoir is simply Q for the reservoir over T for the reservoir. And in this case, it is given to us as 288 Kelvin. So, delta S for the reservoir is 181.2 Joules per Kelvin. So, if you look at the problem it says heat is transferred to ambient which is our reservoir in this case at 288 Kelvin. So, that would be our temperature of the reservoir. So, Q for the reservoir over 288 Kelvin will be 181.2.

(Refer Slide Time: 37:35)



$$\Delta S_{total} = \Delta S_{reservoir} + \Delta S_{system} = 181.2 - 133.8$$

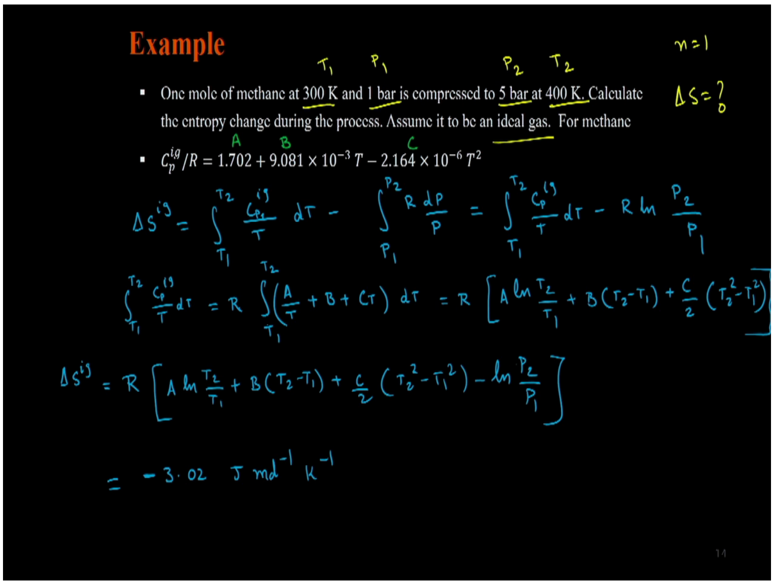
$$= 47.4 \ J \ K^{-1}$$

$$\Delta S_{total} > 0$$

And if we are interested in calculating the total entropy change; delta S total is going to be delta S for the reservoir plus delta S for the system. So, it will be 181.2 minus 133.8 right.

So, that will be 47.4 Joules per Kelvin, this will be delta S total and remember delta S total is greater than 0; as it should be by virtue of due to the second law. So, that completes our problem given an ideal gas I know how to calculate the entropy change for a system and for the surroundings or the reservoir and the total entropy change. Let us quickly look at one other problem in this case we did not do the integral for temperature because there was no temperature change.

(Refer Slide Time: 38:34)



Example

$n = 1$

- One mole of methane at 300 K and 1 bar is compressed to 5 bar at 400 K. Calculate the entropy change during the process. Assume it to be an ideal gas. For methane
- $C_p^{ig}/R = 1.702 + 9.081 \times 10^{-3}\,T - 2.164 \times 10^{-6}\,T^2$

$\Delta S = ?$

$$\Delta S^{ig} = \int_{T_1}^{T_2} \frac{C_p^{ig}}{T}\, dT - \int_{P_1}^{P_2} \frac{R\, dP}{P} = \int_{T_1}^{T_2} \frac{C_p^{ig}}{T}\, dT - R \ln \frac{P_2}{P_1}$$

$$\int_{T_1}^{T_2} \frac{C_p^{ig}}{T}\, dT = R \int_{T_1}^{T_2} \left(\frac{A}{T} + B + CT\right) dT = R \left[A \ln \frac{T_2}{T_1} + B(T_2 - T_1) + \frac{C}{2}\left(T_2^2 - T_1^2\right)\right]$$

$$\Delta S^{ig} = R \left[A \ln \frac{T_2}{T_1} + B(T_2 - T_1) + \frac{C}{2}\left(T_2^2 - T_1^2\right) - \ln \frac{P_2}{P_1}\right]$$

$$= -3.02 \ \mathrm{J\ mol^{-1}\ K^{-1}}$$

So, let us look at another example which involves a calculation with the temperature changes. I have one mole of methane in this case that is compressed from 300 Kelvin, let us use and 1 bar to 5 bar and 400 Kelvin. So, T 1, P 1, T 2, P 2 are given to me I have to calculate the entropy change number of moles is 1 and what is given to me is that we can assume it to be an ideal gas and given the value of Cp i g over R.

Now, remember as we have done earlier for an ideal gas the entropy change is T 1 to T 2; C p ig over T d T minus integral P 1 to P 2 R d P over P. So, this then turns out to be matter of integrating C p by T d T C p ig by T d T minus R ln P 2 over P 1 the second term is pretty straightforward. Remember C p ig is given to us, let us write them down this is A; let us call this coefficients as A, B and C right. So, if I do this integration T 1 to T 2 C p ig by T d T; then it will be remember this is C p ig by R. So, I will get it R there multiplied with the integral of T 1 to T 2; A by T because I am dividing C p ig with T plus B plus CT d T.

And that will be R times A ln; T 2 over T 1 plus B T 2 minus T 1 plus C by 2; T 2 square minus T 1 square right. So, now if I put this back what I have for delta S ig is going to be R times A ln; T 2 over T 1 plus B T 2 minus T 1 plus C by 2, T 2 square minus T 1 square minus ln of P 2 over P 1. I can throw in all the numbers there and the final result is going to be 3.02; it depends on the units I use for R, everything else is dimensionless in this case I have used SI units.

So, delta S ig is going to be in Joules per mole per Kelvin. So, the total entropy change for an ideal gas scenario is going to be negative 3.02 Joules per mole per Kelvin. So, that is how we can calculate an entropy change for an ideal gas given the initial and final conditions; it is pretty straightforward. We just need to perform the integration for C p ig and I need to know the specific heat capacity.

With that we will wind up this lecture; we have looked at the definition for entropy and how to calculate entropy change for a reservoir for a system when we have an ideal gas as the working fluid. And finally, the entropy change of the universe which is that of the system and the surroundings.

Thank you.